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54 A method for the oligomerization of C<sub>2</sub>-C<sub>8</sub>-olefins

57 A method for the oligomerization of C<sub>2</sub>-C<sub>8</sub>-olefins on a heterogeneous catalyst that contains nickel, consisting of i) a preparatory catalyst treatment phase, in which the catalyst is brought into contact with a first hydrocarbon mixture exhibiting an olefin content of less than 50% by weight and a diolefin content and alkyne content of less than 0.1% by weight, and of ii) an essentially stationary operating phase, in which a flow of a second hydrocarbon mixture exhibiting a C<sub>2</sub>-C<sub>8</sub>-olefin content of between 50 and 100% by weight and a diolefin and alkyne content of less than 10% by weight is brought into contact with the catalyst.

## Description

This invention concerns a method for the oligomerization of C<sub>2</sub>-C<sub>8</sub>-olefins on a heterogeneous catalyst that contains nickel.

Olefins with between 2 and 8 carbon atoms or their mixtures are available in large quantities from FCC-units (Fluidized Catalyst Cracking) and also from steam crackers. It is known to use the respective C<sub>4</sub>-section, i.e., a mixture that basically consists of butenes and butanes, for the production of oligomers and particularly of octenes and dodecenes after the iso-butene has been separated. After a hydroformylation and subsequent hydration to form the respective alcohols, octenes as well as dodecenes are used for the production of softening agents or tenside alcohols.

The large-scale oligomerization is run under a homogeneous or heterogeneous catalysis. The homogeneously catalyzed method exhibits the disadvantage that the catalyst must be separated from the reaction mixture. This separation phase forms waste flows that are expensive to process. Furthermore, it is impossible to regenerate the homogeneous catalyst.

The above-described disadvantages do not exist for the heterogeneously catalyzed olefin oligomerization. The most important heterogeneously catalyzed olefin oligomerization methods used by the industry are listed, for example, in A. Chauvel and G. Lefebvre, *Petrochemical Process*, Edition Technip (1989), page 183-187 and in F. Asinger, *The Petrochemical Industry*, Akademie-Verlag (1971), page 278-299.

From DE-43 39 713 is known a method for the oligomerization of linear C<sub>2</sub>-C<sub>8</sub>-olefins on a solid bed catalyst at an increased pressure and an increased temperature, in which case the substantially active components of the catalyst consist of between 10 and 70% by weight nickel oxide, between 5 and 30% by weight titanium dioxide and/or zircon dioxide, between 0 and 20% by weight aluminum oxide and the rest of silicon oxide. The oligomerization of butene can be performed with this method at a very high selectivity in relation to linear products. In document DE-43 39 713, there is a recommendation to expose the freshly produced catalyst to conditioning in a dry nitrogen flow prior to its use, e.g., at the atmospheric pressure and at temperatures of between 200 and 500 °C to remove water that may still be present in the catalyst. It was found that the catalyst service life can be improved, particularly in the case the method in accordance with DE-43 39 713 is run in an adiabatic manner.

Accordingly, the task of this invention consists in proposing a method for the oligomerization of C<sub>2</sub>-C<sub>8</sub>-olefins on a heterogeneous catalyst that contains nickel to achieve the longest-possible catalyst service life.

It was surprising to find that the catalyst service life can be extended substantially when the freshly produced or conditioned catalyst undergoes - prior to bringing it into contact with the mixture to be used - a preparatory treatment, in which the catalyst is brought into contact with a hydrocarbon mixture that contains fewer olefins than the mixture to be used.

Accordingly, the object of the invention consists of a method for the oligomerization of C<sub>2</sub>-C<sub>8</sub>-olefins on a heterogeneous catalyst that contains nickel, in which case the method includes a preparatory catalyst treatment phase, in which the catalyst is brought into contact with a first hydrocarbon mixture exhibiting an olefin content of less than 50% by weight and a diolefin and alkyne content of less than 0.1% by weight (hereinafter called "olefin-poor hydrocarbon mixture"), and includes a preferably and basically stationary operating phase, in which the catalyst is brought into contact with a flow of a second hydrocarbon mixture with a C<sub>2</sub>-C<sub>8</sub>-olefin content of between 50 and 100% by weight and a diolefin and alkyne content of less than 10 ppm by weight (hereinafter called "olefin-rich hydrocarbon mixture"). It is preferred to let the flow of the olefin-rich hydrocarbon mixture displace the olefin-poor hydrocarbon mixture. In that respect, the preparatory catalyst treatment phase is shorter than the operating phase, e.g., a preparatory catalyst treatment phase of between 12 and 72 hours in comparison with an operating period of between 1 and 2 years. It is generally preferred that the olefin-poor and olefin-rich hydrocarbon mixtures basically consist of hydrocarbons with the same number of C-atoms. The olefin-poor and olefin-rich hydrocarbon mixtures basically and particularly consist of C<sub>4</sub>-hydrocarbon mixtures.

The term "hydrocarbon mixture" will be used here, since the hydrocarbon flows that are available on a large scale and are used to run the method in accordance with the invention do indeed generally consist of mixtures. It is understood that the method in accordance with the invention can also be performed with pure hydrocarbons that meet the indicated conditions.

The method in accordance with the invention may include an intermediate phase between the preparatory catalyst treatment phase and the operating phase, in which the catalyst is brought into contact with a hydrocarbon mixture exhibiting a composition that changes from an olefin-poor hydrocarbon mixture to an olefin-rich hydrocarbon mixture in a continuous or a step-by-step manner. A basically stationary operation is maintained during the operating phase. "Basically stationary" means that the composition of the educt and product flows is maintained as constant as possible, i.e., with the exception of natural fluctuations.

The preparatory catalyst treatment phase and operating phase can be executed separately with respect to space and/or time. This case occurs regularly, for example, when there exists a time-related and/or space-related connection between the preparatory catalyst treatment phase and the catalyst production phase. In such a case, it is preferred that the catalyst remain covered with an olefin-poor hydrocarbon mixture during transport and/or storage. It is basically preferable, however, that the preparatory catalyst treatment phase and the operating phase be run in the same reactor. Furthermore, it is preferred that the preparatory catalyst treatment phase be performed - preferably including a catalyst-conditioning that will be described later - immediately prior to the start of the operating phase.

The usable and heterogeneous catalysts that contain nickel may exhibit different structures. One basically takes into consideration known catalysts such as those described in C.T. O'Connor et al., *Catalysis Today*, Vol. 6 (1990), page 336-338. Nickel catalysts bonded to carriers are used in particular. The carrier materials may consist of silicic acid, oxide of aluminum, alumino silicates, alumino silicates with layer structures and of zeolites such as mordenite, faujasite, zeolite X, zeolite Y and ZSM-5, zirconium oxide treated with acids or sulfated titanium dioxide. Particularly suited are precipitation catalysts that are obtainable by mixing aqueous solutions of nickel salts and silicates

such as sodium silicate with nickel nitrate and possibly aluminum salts such as aluminum nitrate, followed by a calcining. Catalysts that are obtained by incorporating  $\text{Ni}^{2+}$ -ions by way of an ion exchange in natural and/or synthetic layer silicates such as montmorillonite can be used. Suitable catalysts can also be obtained by impregnating acidic acid, aluminum or alumo silicates oxides with aqueous solutions of soluble nickel salts such as nickel nitrate, nickel sulfate or nickel chloride, followed by a calcination.

Preference is given to catalysts that contain nickel oxide. Particularly preferred are catalysts that basically consist of  $\text{NiO}$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$  and/or  $\text{ZrO}_2$  as well as possibly of  $\text{Al}_2\text{O}_3$ . Such catalysts are particularly preferred when the method in accordance with the invention is used for the oligomerization of butene. They lead to a preference for a dimerization regarding the formation of higher oligomers and they mostly deliver linear products. Mostly preferred is a catalyst whose active components consist of between 10 and 70% by weight nickel oxide, between 5 and 30% by weight titanium dioxide and/or zircon dioxide, between 0 and 20% by weight aluminum oxide and the rest of silicon oxide. Such a catalyst can be obtained by precipitating the catalyst mass at a pH-value of between 5 and 9 by adding an aqueous solution containing nickel nitrate to an alkali water glass solution that contains titanium dioxide and/or zirconium dioxide, followed by a filtering, drying and tempering at between 350 and 650 °C. Reference is made here to DE-43 39 713 for details regarding the production of these catalysts. Reference is also made to the full content of the disclosure in this document and the prior art cited therein.

The catalyst is preferably available in solid pieces such as in the form of pellets with a diameter of between 2 and 6 mm and a height of between 3 and 5 mm, in the form of rings with an outside diameter of between 5 and 7 mm, a height of between 2 and 5 mm and a hole diameter of between 2 and 3 mm or in the form of strands of different lengths and with a diameter of between 1.5 and 5 mm. Such forms are obtained in a generally known manner by pellet-compressing or extrusion and in most cases with the help of a pellet-compressing agent such as graphite or stearic acid.

The method in accordance with the invention is based on a freshly produced, regenerated or conditioned catalyst. The production of suitable catalysts has been described earlier and is basically known. Immediately after its manufacture and particularly when the production ends with a heat treatment phase, the catalyst is in a high activity state. The regeneration of a used catalyst to again reach a high activity level can be achieved with the so-called "burning off", i.e., by heating the catalyst in a gas mixture that contains oxygen such as a mixture of  $\text{O}_2$  and  $\text{N}_2$  to a temperature of 300-600 °C. The ratio between  $\text{O}_2$  and  $\text{N}_2$  in the given mixture is in an advantageous manner selected such that the heat of reaction formed during the treating of the used catalyst is less than 50 °C.

It is generally preferred to condition the catalyst within the scope of the preparatory catalyst treatment phase prior to bringing it into contact with the olefin-poor hydrocarbon mixture. To do so, the catalyst can be heated in the presence of an inert gas to a temperature of more than 100 °C and preferably of between 150 and 500 °C. The heating process may last from a few hours to many days such as between 6 and 150 hours and preferably between 12 and 72 hours. An inert gas that may be at a normal or higher pressure preferably flows through the catalyst material. The inert gas may consist of gases that essentially experience no chemical conversion at the conditioning temperature and essentially experience no chemical or physical interaction with the catalyst. Nitrogen, argon or neon are suitable gases. After the heating, the catalyst is preferably permitted to cool in an inert gas flow, preferably to a temperature of less than 40 °C.

It is advantageous to perform the conditioning and the bringing-into-contact with the hydrocarbon mixture in the same reactor.

In accordance with the invention, the catalyst undergoes a preparatory treatment phase prior to bringing it into contact with the actual product application mixture. During the preparatory treatment, the catalyst is brought into contact with a hydrocarbon mixture that has an olefin content of less than 50% by weight. The olefin-poor hydrocarbon mixture preferably contains less than 45% by weight, particularly less than 25% by weight and particularly preferred less than 10% by weight of olefins. It is generally possible to obtain olefin contents down to 3% by weight on a large-scale basis and those are thus preferred. 50% by weight or more, preferably 75% by weight or more and particularly 90% by weight or more of the olefin-poor hydrocarbon mixture consists of hydrocarbons that are not accessible to an oligomerization on the heterogeneous catalyst such as alkanes, for example, propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane and/or dodecane. The mixture particularly and essentially consists of 95% by weight or more of C<sub>4</sub>-hydrocarbons. The olefin-poor hydrocarbon mixture contains less than 0.1% by weight, particularly less than 100 ppm by weight and particularly preferred less than 50 ppm by weight of diolefins and/or alkynes, and it preferably and basically contains no diene and alkyne. As is described later in connection with the olefin-rich mixture, the removal of dienes and alkynes can be achieved through a selective hydration, for example.

The boiling range (at 1 atm) of the olefin-poor hydrocarbon mixture generally varies between -50 °C and 250 °C, particularly between -20 °C and 80 °C and particularly preferred between -15 °C and 10 °C.

Bringing the catalyst into contact with the olefin-poor hydrocarbon mixture preferably occurs at a pressure of between 1 and 4 bar and can be executed at a temperature of between 10 and 100 °C, preferably of less than 70 °C and particularly preferred at less than 40 °C. To bring it into contact with the catalyst, the olefin-poor hydrocarbon mixture may be in the gaseous phase or also in the liquid phase. It is preferred to perform the preparatory catalyst treatment under such conditions that the olefin-poor hydrocarbon mixture is available in the liquid phase.

An olefin-poor hydrocarbon mixture that can serve the purpose of a suitable hydrocarbon mixture for this invention can be obtained, for example, with a full hydration of a C<sub>4</sub>-flow from a FCC-unit or a steam cracker. Field butanes can be used as well.

The preparatory catalyst treatment phase can be executed prior or after the catalyst is installed in the reactor. In a particularly preferred example of the invention, the catalyst is brought into contact with the olefin-poor hydrocarbon mixture after being installed in the reactor.

The hydrocarbon mixtures that are available on a large scale and are suitable as olefin-poor hydrocarbon mixtures for the purpose of this invention mostly contain compounds that act as catalyst poisons and deactivate the oligomerization catalyst. This includes oxygen-containing compounds such as alcohol, aldehydes, ketones and ethers as well as nitrogen-containing, sulfur-containing and halogen-containing compounds. The presence of such catalyst poisons during the preparatory catalyst treatment phase would lead to an undesirable decrease in the catalyst activity level.

For that reason and according to a preferred aspect of the invention, the olefin-poor hydrocarbon mixture is passed across an adsorption agent to remove catalyst poisons prior to bringing it into contact with the catalyst. A suitable adsorption agent consists of molecular sieves, preferably with a pore diameter of more than 4 Å to 15 Å. Molecular sieves may consist of crystalline, natural aluminum silicates such as layer lattice silicates as well as synthetic molecular sieves. Also suited are commercially available molecular sieves such as the types manufactured by the companies Bayer AG, Dow, Union Carbide, Laporte or Mobil. These molecular sieves may be zeolite of the types A, X and Y. Also suitable are synthetic molecular sieves that in addition to silicon and aluminum as main components also contain other atoms as secondary components. These may be incorporated in the zeolites by way of an ion exchange with exchangeable cations. An exchange with rare earths such as gallium, indium or lanthanum, or with nickel, cobalt, copper, zinc or silver shall be listed here as examples.

Furthermore, it is also possible to use synthetic zeolites, in which other atoms such as boron or phosphorous have been incorporated in the lattice through co-precipitation.

Further suitable adsorption agents consist of aluminum oxide, aluminum phosphate, silicon dioxide, siliceous earth, titanium dioxide, zircon dioxide, polymeric adsorption agents and mixtures thereof. The passing of the olefin-poor hydrocarbon mixture across the adsorption agent is appropriately achieved on a solid bed or moving bed. The olefin-poor hydrocarbon mixture may be in the gaseous or liquid state when passing across the adsorption agent; the liquid phase is preferred, however.

The concentration of compounds that contain oxygen, nitrogen, sulfur and halogen in the olefin-poor mixture preferably - possibly after the cleaning phase described above - amounts to less than 1 ppm by weight and particularly to less than 0.5 ppm by weight.

In a preferred manner, the contact between the catalyst and the olefin-poor hydrocarbon mixture is achieved by letting the olefin-poor hydrocarbon mixture flow through the catalyst fill, i.e., preferably under adiabatic conditions. Heat is generally released when the catalyst comes into contact with the olefin-poor hydrocarbon mixture. In the adiabatic operation, the thus formed heat must be removed by the olefin-poor hydrocarbon mixture. It is preferred to introduce the olefin-poor hydrocarbon mixture at a temperature of between 10 °C and less than 60 °C and preferably of less than 40 °C and to continue the flowthrough until the temperature in the catalyst fill has been lowered to less than 60 °C and particularly to less than 40 °C.

After the contact with the catalyst, the olefin-poor hydrocarbon mixture can be completely or partly returned - possibly after cooling it - and may be mixed with a fresh olefin-poor hydrocarbon mixture. It is finally piped out of the process and discarded. It may be burned or piped to a steam cracker.

After the preparatory catalyst treatment phase is completed, the catalyst is, during the operating phase, brought into contact with a hydrocarbon mixture flow with a C<sub>2</sub>-C<sub>8</sub>-content of between 50 and 100% by weight and preferably of between 60 and 100% by weight. The olefin percentage content generally consists of an olefin such as propylene or a mixture of olefins with the same number of C-atoms, such as isomeric butene. The oligomerization, particularly the dimerization

or trimerization, of the C<sub>2</sub>-C<sub>8</sub>-olefins that are contained in the olefin-rich hydrocarbon mixture occurs in the operating phase. In addition to the C<sub>2</sub>-C<sub>8</sub>-olefins, the olefin-rich hydrocarbon mixture may also have an inert percentage content that is not accessible to the oligomerization. This inert percentage content may consist of saturated hydrocarbons such as alkanes and/or cyclo-alkanes. The saturated hydrocarbons generally have the same number of C-atoms than the olefin or a C-atom number that is higher or lower by one C-atom.

A preferred olefin-rich mixture contains between 50 and 100% by weight and preferably between 60 and 90% by weight butene and between 0 and 50% by weight and preferably between 10 and 40% by weight butane. The butene fraction preferably includes less than 5% and particularly preferred less than 3% by weight iso-butene (in relation to the butene fraction). The butene fraction generally has the following composition (in relation to the butene fraction):

1-butene:	1 to 50% by weight
cis-2-butene:	1 to 50% by weight
trans-2-butene:	1 to 99% by weight
iso-butene:	1 to 5% by weight

A particularly preferred application material is formed by the so-called Raffinate II that consists of an iso-butene-depleted C<sub>4</sub>-section from an FCC-unit or a steam cracker. Raffinate II has the following typical composition:

i- and n-butene:	26% by weight
i-butene:	1% by weight
1-butene:	26% by weight
trans-2-butene:	31% by weight
cis-2-butene:	16% by weight

When diolefins or alkynes are present in the olefin-rich hydrocarbon mixture, they are removed from the mixture to less than 10 ppm by weight prior to the oligomerization. They are preferably removed through a selective hydration according to EP-81041 and DE-15 68 542 and in a particularly preferred manner through a selective hydration to a residual content of less than 5 ppm by weight and particularly of less than 1 ppm by weight.

Furthermore and in an appropriate manner, oxygen-containing compounds such as alcohols, aldehydes, ketones or ethers are almost completely removed from the olefin-rich hydrocarbon mixture. To achieve this, the olefin-rich hydrocarbon mixture can be passed in an advantageous manner across an adsorption agent such as a molecular sieve and particularly a sieve with a pore diameter of > 4 Å to 5 Å. Reference is hereby made to the above text in relation to the olefin-poor hydrocarbon mixture. The concentration of oxygen-containing, nitrogen-containing and halogen-containing compounds in the olefin-rich hydrocarbon mixture is preferably less than 1 ppm by weight and particularly less than 0.5 ppm by weight.

The preferred operating phase is run at temperatures of between 30 and 280 °C, particularly of between 30 and 140 °C and particularly preferred of between 40 and 130 °C. It is preferably performed at a pressure of between 10 and 300 bar, particularly of between 15 and 100 bar and

particularly preferred of between 20 and 80 bar. In that respect, the pressure is appropriately set such that the olefin-rich hydrocarbon mixture is in the liquid or supercritical state at the selected temperature.

The expert knows of suitable and possibly pressure-proof reaction equipment to bring the hydrocarbon mixture into contact with the heterogeneous catalyst. This includes the generally used reactors for gas/solid reactions or liquid/solid reactions. Tube bundle reactors or shaft kilns can be used. Shaft kilns are preferred because of their lower costs. The oligomerization process in accordance with the invention can be performed in a single reactor, in which case the oligomerization catalyst can be arranged on a single or on several solid beds in the reactor. As an alternative, the method in accordance with the invention can also be run in a reactor cascade consisting of several and preferably of two reactors arranged in series; when passing the reactor or reactors located upstream of the last cascade reactor, it is possible to run the olefin oligomerization in the reaction mixture only to reach a partial conversion level and the desired final conversion level will be achieved only after the reaction mixture has passed through the last cascade reactor. The oligomerization catalyst can be arranged on a single or on several solid catalyst beds in the individual reactors of the reactor cascade. Furthermore, different reaction conditions regarding pressure and/or temperature can be set in the reactors of the reactor cascade within the scope of the above-mentioned pressure and temperature ranges. Although it is preferred to use the same catalyst in all cascade reactors, it is also possible to use different oligomerization products in the individual cascade reactors. The preferred reactor basically consists of a vertical cylindrical pipe that holds the catalyst and through which the olefin-rich hydrocarbon mixture flows from the top to the bottom, for example.

After exiting the reactor or the last cascade reactor, the formed oligomers are separated from the unreacted olefins and the saturated hydrocarbons. The formed oligomers can be purified in a subsequent vacuum fractionation phase.

In a preferred implementation, the reaction discharge that does not contain any of the formed oligomers and basically consists of unreacted olefins and saturated hydrocarbons is completely or partially returned. It is preferred to select the return ratio in such a manner that the oligomer concentration in the reaction mixture does at no point in the reactor (or the reactor cascade) exceed 35% by weight and preferably 20% by weight in relation to the reaction hydrocarbon mixture.

It is advantageous to perform the operating phase in an adiabatic manner. The oligomerization reaction is generally exothermal. Accordingly, the reaction mixture experiences a temperature increase when flowing through the catalyst bed. In contrast to an isothermal reaction, in which the heat quantity formed in an exothermal reaction is removed through a cooling with cooling or thermostat devices to maintain the reactor temperature at a constant level, i.e., isotherm, an adiabatic reaction refers to an operation, in which the heat released during an exothermal reaction is absorbed by the reaction mixture in the reactor and no cooling through cooling devices occurs. It is understood that a negligibly small part of the heat released during the exothermal reaction is also and unavoidably absorbed by the reactor body and is released to the environment through heat conduction and dissipation. Accordingly and from a technical point of view, an adiabatic reaction or operation is understood to indicate a reaction or operation, in which the whole reaction heat is absorbed by the reaction mixture and is removed with the mixture from the reactor, i.e., with the exception of the reaction heat part that is transferred from the reactor to the environment through a natural heat



conduction and dissipation. There basically exist two possibilities to control the reaction temperature. Since the exothermal reaction is created by the contact between olefins and catalyst in the case of this oligomerization process and heat is thus released only in the area of the catalyst fill, the reaction temperature can be controlled by setting the olefin concentration in the supplied hydrocarbon mixture. This mixture itself will be appropriately controlled by returning the unreacted olefins that have been separated from the oligomeric product and the saturated hydrocarbons to the oligomerization reactor. Since the flow returned to the oligomerization reactor exhibits a lower content of reactive olefins and a higher content of hydrocarbons that have been saturated in an inert manner under the reaction conditions than the freshly supplied hydrocarbon flow, the return flow mixed with this flow leads to a diluting of the olefin content. Accordingly, the reactor temperature can be directly controlled with the ratio between return flow and fresh hydrocarbon flow.

A further possibility to control the process consists in controlling the inlet temperature of the hydrocarbon mixture. A lower temperature in the supplied hydrocarbon mixture leads to an improved reaction heat removal. On the other hand and in the case of a decreasing catalyst activity level, it is possible to increase the inlet temperature of the hydrocarbon mixture to achieve a higher reaction velocity and to thus make up for the decreasing catalyst activity level. The inlet temperature of the hydrocarbon mixture is generally limited by safety aspects and practical considerations. The maximum inlet temperature is generally 130 °C for a hydrocarbon mixture that contains mostly butene and possibly butane. The catalyst is exhausted and must be replaced with a new catalyst when the maximum inlet temperature has been reached for the olefin-rich hydrocarbon mixture. The exhausted catalyst can be regenerated.

The operating phase of the method in accordance with the invention is preferably controlled such that the heat of reaction above a catalyst bed does not exceed 50 °C, particularly 40 °C and particularly preferred 30 °C. Heat of reaction is defined as the difference between the inlet temperature of the hydrocarbon mixture and the outlet temperature of the reaction mixture. The adiabatic operation also includes a process configuration of the method in accordance with the invention, in which the olefin conversion to form oligomers is distributed to two or more, preferably two, oligomerization reactors and the partially reacted reaction mixture is cooled with conventional cooling devices such as cooling jackets after exiting one reactor and prior to entering the next cascade reactor.

With a suitable operation, it is possible to achieve a reaction rate of between 15 and 50% by weight in relation to the olefin percentage content of the hydrocarbon mixture.

The invention will be explained in more detail with the following examples:

#### Reference example

A catalyst produced in accordance with DE-43 39 713 in the form of pellets measuring 5 mm x 5 mm was filled into an adiabatic reactor (4 m long, 80 cm diameter). (Composition in % by weight of the active component: NiO 50% by weight, TiO<sub>2</sub> 12.5% by weight, SiO<sub>2</sub> 33.5% by weight, Al<sub>2</sub>O<sub>3</sub> 4% by weight).

The catalyst was first conditioned with a dry N<sub>2</sub> flow for 24 h at 160 °C and was then cooled to 25 °C in a nitrogen flow. The catalyst was then flushed at a pressure of 4 bar with a hydrocarbon mixture exhibiting the composition indicated below and a temperature of 25 °C:

i-butane:	2% by weight
n-butane:	10% by weight
i-butene:	2% by weight
1-butene:	32% by weight
trans-2-butene:	37% by weight
cis-2-butene:	17% by weight
diolefins+alkynes:	<1 ppm by weight

In that manner occurred a temperature increase to 195 °C within 120 minutes. The supply of the fresh hydrocarbon mixture was then interrupted. The reactor discharge was cooled to cool the reactor, the formed oligomers were removed and the reactor discharge containing no oligomers was returned and fed again to the reactor. The return of the cooled discharge containing no oligomers was continued until the reactor had cooled down to 25 °C. After the cooling phase to 25 °C, a mixture of the above-described composition was again passed across the catalyst at a rate of 15 kg/h. The temperature of the supplied mixture was increased until a butene reaction of 25% was found in the reaction discharge. This required an inlet temperature of 90 °C.

After the plant was shut down, the catalyst was removed and an increase in the C-content from 3.3% by weight in the fresh catalyst to 11.2% by weight in the removed sample was noted.

#### Example in accordance with the invention

The reactor and catalyst described in the previous example were used.

The catalyst was first conditioned with a dry N<sub>2</sub> flow for 24 h at 160 °C and was then cooled to 25 °C in a nitrogen flow. The catalyst was then flushed at a pressure of 4 bar with a mixture exhibiting the composition indicated below and a temperature of 25 °C:

i-butane:	10% by weight
n-butane:	50% by weight
i-butene:	1% by weight
1-butene:	2% by weight
trans-2-butene:	30% by weight
cis-2-butene:	7% by weight
diolefins+alkynes:	<50 ppm by weight

In that manner occurred a temperature increase of 20 °C within 3 hours. The catalyst was flushed with the above-described mixture for 2 h until the temperature of the exiting mixture had reached 25 °C. A mixture of the following composition was then passed across the catalyst at a throughput of 15 kg/h.

i-butane:	2% by weight
n-butane:	10% by weight
i-butene:	2% by weight
1-butene:	32% by weight
trans-2-butene:	37% by weight
cis-2-butene:	17% by weight
dioléfins+alkynes:	<1 ppm by weight

The temperature of the supplied mixture was increased until a butene reaction of 25% was found in the reaction discharge. This required an inlet temperature of 40 °C. The inlet temperature that was lower than that for the reference example to achieve the same conversion rate pointed to the higher activity level of the catalyst that was pretreated in accordance with the invention. The initially low inlet temperature led to a catalyst service life that was 8 times longer than that found for the reference example.

After the plant was shut down, the catalyst was removed and an increase in the C-content from 3.3% by weight in the fresh catalyst to 7.9% by weight in the removed sample was noted.

## Patent claims

1. A method for the oligomerization of C<sub>2</sub>-C<sub>8</sub>-olefins on a heterogeneous catalyst that contains nickel, consisting of
  - i) a preparatory catalyst treatment phase, in which the catalyst is brought into contact with a first hydrocarbon mixture exhibiting an olefin content of less than 50% by weight and a diolefin content and alkyne content of less than 0.1% by weight, and of
  - ii) an operating phase, in which a flow of a second hydrocarbon mixture exhibiting a C<sub>2</sub>-C<sub>8</sub>-olefin content of between 50 and 100% by weight and a diolefin and alkyne content of less than 10% by weight is brought into contact with the catalyst.
2. A method in accordance with claim 1, in which the catalyst is heated to a temperature of more than 100 °C with the first hydrocarbon mixture in the presence of an inert gas and prior to bringing it into contact.
3. A method in accordance with claim 1 or 2, in which the preparatory catalyst treatment phase and operating phase are run in the same reactor.
4. A method in accordance with one of claims 1 through 3, in which the catalyst contains nickel oxide.
5. A method in accordance with claim 4, in which the catalyst essentially consists of NiO, SiO<sub>2</sub>, TiO<sub>2</sub> and/or ZrO<sub>2</sub> as well as possibly Al<sub>2</sub>O<sub>3</sub>.
6. A method in accordance with one of the previous claims, in which the first hydrocarbon mixture and the flow of the second hydrocarbon mixture are passed across an adsorption material prior to bringing them into contact with the catalyst.
7. A method in accordance with one of the previous claims, in which the operating phase is performed at such a pressure that ensures a liquid phase for the flow of the second hydrocarbon mixture.
8. A method in accordance with one of the previous claims, in which the flow of the second hydrocarbon mixture contains the following substances as major components:
  - 50 to 100% by weight butene and
  - 0 to 50% by weight butane.
9. A method in accordance with one of the previous claims, in which the first hydrocarbon mixture essentially consists of C<sub>4</sub>-hydrocarbons.
10. A method in accordance with one of the previous claims, in which the preparatory catalyst treatment phase and the operating phase are run in an adiabatic reactor or in a cascade of adiabatic reactors arranged in series.

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